

Corrosion.

(1) When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called **corrosion**. Almost all metals except the least active metals such as gold, platinum and palladium are attacked by environment i.e., undergo corrosion. For example, silver tarnishes, copper develops a green coating, lead or stainless steel lose their luster due to corrosion. Corrosion causes enormous damage to building, bridges, ships and many other articles made of iron.

Thus **corrosion** is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.

In case of iron, corrosion is called rusting. Chemically, rust is hydrated form of ferric oxide, $Fe_2O_3 \cdot xH_2O$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air. It has been observed that rusting takes place only when iron is in contact with moist air. Iron does not rust in dry air and in vacuum.

(2) **Factors which affect corrosion:** The main factors which affect corrosion are

(i) **Position of metals in emf series:** The reactivity of metal depends upon its position in the electrochemical series. More the reactivity of metal, the more will be the possibility of the metal getting corroded.

(ii) **Presence of impurities in metals:** The impurities help in setting up voltaic cells, which increase the speed of corrosion

(iii) **Presence of electrolytes:** Presence of electrolytes in water also increases the rate of corrosion. For example, corrosion of iron in sea water takes place to larger extent than in distilled water.

(iv) **Presence of CO_2 in water:** Presence of CO_2 in natural water increase rusting of iron. Water containing CO_2 acts as an electrolyte and increases the flow of electrons from one place to another

(v) **Presence of protective coatings:** When the iron surface is coated with layers of metals more active than iron, then the rate of corrosion is retarded. For example, coating of zinc on iron prevents rusting.

(vi) **Temperature:** A rise in temperature (within a reasonable limit) increases the rate of corrosion.

(3) **Classification of corrosion process:** Depending upon the nature of corrosion, and the factors affecting it, the corrosion may be classified as follows.

(i) **Chemical corrosion:** Such corrosion, generally takes place when

(a) Reactive gases come in contact with metals at high temperatures e.g., corrosion in chemical industry.

(b) Slow dissolution of metal takes place when kept in contact with non-conducting media containing organic acids.

(ii) **Bio-chemical corrosion or Bio-corrosion:** This is caused by the action of microorganisms. Soils of definite composition, stagnant water and certain organic products greatly favor the bio-corrosion.

(iii) **Electrochemical corrosion:** It occurs in a gaseous atmosphere in the presence of moisture, in soils and in solutions. For example, the following corrosions are electrochemical in nature:

- (a) Corrosion of insoluble anodes
- (b) Corrosion of pipelines with current carrying liquids flowing through them.
- (c) Corrosion of underground metal structure

(4) **Mechanism of rusting of iron: Electrochemical theory of rusting.** The phenomenon of corrosion can be explained with the help of electrochemical theory which involves oxidation and reduction reactions. According to electrochemical theory of corrosion, it is believed that non-uniform surface of metal or impurities present in iron behave like small electric cells (**called corrosion couples**) in the presence of water containing dissolved oxygen or carbon dioxide. A film of moisture with dissolved CO_2 constitutes electrolytic solution covering the metal surface at various places. The schematic representation of mechanism of rusting of iron is shown in Fig.

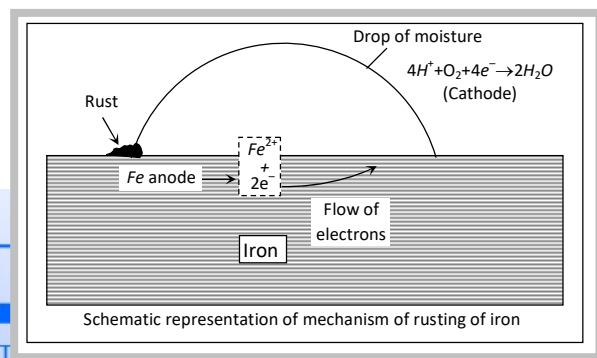
In the small electrolytic cells, pure iron acts as anode while cathodes are impure portions. The overall rusting involves the following steps,

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidized to ferrous ions.

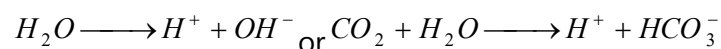
At anode: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$.

Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.

(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^{+} ions are



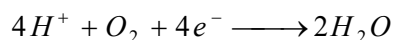
obtained either from water or from acidic substances (e.g. CO_2) in water



At cathode: $H^+ + e^- \longrightarrow H$

The hydrogen atoms on the iron surface reduce dissolved oxygen. $4H + O_2 \longrightarrow 2H_2O$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as,



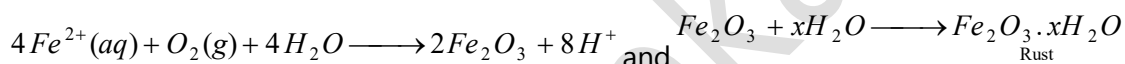
(iii) The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalize number of electrons lost and gained i.e.

Oxidation half reaction : $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-] \times 2$ ($E^- = -0.44 V$)

Reduction half reaction : $4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$ ($E^- = 1.23 V$)

Overall cell reaction : $2Fe(s) + 4H^+ + O_2 \longrightarrow 2Fe^{2+}(aq) + 2H_2O$ ($E_{cell}^- = 1.67 V$)

The ferrous ions are oxidized further by atmospheric oxygen to form rust.



It may be noted that salt water accelerates corrosion. This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.

(5) **Corrosion protection:** Corrosion of metals can be prevented in many ways. Some commonly used methods are described below.

(i) **By surface coating:** Corrosion of metals can be prevented by coating their surfaces with any of the following

(a) By applying, oil, grease, paint or varnish on the surface.

(b) By coating/depositing a thin layer of any other metal which does not corrode. For example, iron surface can be protected from corrosion by depositing a thin layer of zinc, nickel or chromium on it. Copper/brass can be protected by coating it with a thin layer of tin. Tinning of brass utensils is a very common practice in our country.

(c) By Galvanization: Prevention of corrosion of iron by Zn coating.

(ii) **By connecting metal to a more electropositive metal:** A metal can be protected from corrosion by connecting it to a more electropositive metal. As long as the more electropositive metal is there, the given metal does not get corroded. For example, iron can be protected from corrosion by connecting it to a block/plate of zinc or magnesium. This method of corrosion protection is called **cathodic protection**.



(iii) **By forming insoluble phosphate or chromate coating:** Metal surfaces are treated with phosphoric acid to form an insoluble phosphate **by connecting metal to a more** coating on the surface. This phosphate coating protects the metal from corrosion. Formation of a thin chromate layer also prevents the corrosion of metals.

(iv) **Using anti – rust solutions:** To retard the corrosion of iron certain anti – rust solutions are used. For example, solutions of alkaline phosphates and alkaline chromates are generally used as anti – rust solutions. Due to the alkaline nature of these solutions, the H^+ ions are removed from the solutions, and

rusting is prevented. For example, iron articles are dipped in boiling alkaline sodium phosphate solutions, when a protective insoluble sticking film of iron phosphate is formed.

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